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Pressure Effects on the Intervalence-Transfer Band of Salts of Mixed-Valence 1′,1‴-Disubstituted Biferrocenium Cations

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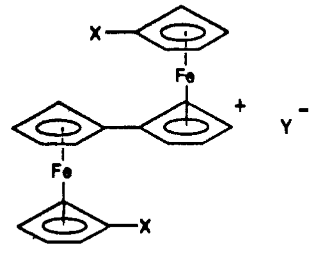
Abstract: The pressure dependence of the intervalence-transfer (IT) electronic absorption band has been determined for the mixed-valence biferrocenium and 1′,1‴-diethylbiferrocenium cations intercalated into a clay and for the following eight microcrystalline compounds: biferrocenium triiodide (**1**); biferrocenium hexafluorophosphate (**2**); 1′,1‴-diiodobiferrocenium triiodide (**3**); 1′,1‴-diiodobiferrocenium dibromoiodate (**4**); 1′,1‴-dibromobiferrocenium triiodide (**5**); 1′,1‴-dichlorobiferrocenium triiodide hemiiodine (**6**); 1′,1‴-diethylbiferrocenium triiodide (**7**); 1′,1‴-di-*n*-butylbiferrocenium triiodide (**8**). Basically three different types of pressure dependencies of the energy of the IT band are seen. Compounds **3**–**5**, which have a solid-state packing arrangement consisting of alternating stacks of cations and anions, exhibit one type of behavior. For these three compounds the IT band shifts blue initially with pressure, and above ~80 kbar there is the onset of a rather abrupt reversal where the IT band shifts red with increasing pressure. The initial blue shift is probably attributable to an increase in the zero-point energy difference between the two vibronic states of the mixed-valence cation, reflecting interactions of the cation with its environment. The red shift of the IT band at high pressures may be attributable to a reduction of the vibronic coupling in the cation. The other microcrystalline compounds (**1**, **2**, **6**–**8**), some of which have a segregated cation stack type of packing, do not show the initial blue shift of the IT band at low pressures, but do show to variable degrees the red shift at high pressures. The zero-point energy differences are apparently already saturated at ambient pressures for these compounds. The clay-intercalated mixed-valence cations show the third behavior, where there is no red shift at high pressures, just a blue shift of the IT band throughout a large range of pressures. The absence of a red shift of the IT band at high pressures is rationalized by an absence of attenuation of vibronic coupling in the mixed-valence cation due to its orientation in the clay interlamellar region.



1, X = H; $Y^- = I_3^-$
2, X = H; $Y^- = PF_6^-$
3, X = I; $Y^- = I_3^-$
4, X = I; $Y^- = IBr_2^-$
5, X = Br; $Y^- = I_3^-$
6, X = Cl; $Y^- = I_3^- \cdot 1/2 I_2$
7, X = Et; $Y^- = I_3^-$
8, X = n-Bu; $Y^- = I_3^-$

The study of intramolecular electron-transfer processes involving binuclear mixed-valence complexes in the *solid state* can directly give fundamental information about environmental control of the rate of electron transfer. Complexes such as **1**–**8** are proving to be very useful in such a pursuit. Complex **6** is relatively valence trapped with an electron-transfer rate characterized by $k < 10^6$ s^{-1} at 350 K, as judged by ^{57}Fe Mössbauer data.[3] On the other hand, complexes **3** and **5** are valence detrapped on the ^{57}Fe Mössbauer and EPR time scales at 4.2 K.[3] Thus, **3** and **5** have $k > 10^9$ s^{-1} at 4.2 K. This very appreciable change in intramolecular electron-transfer rate has been shown[3,4] to be attributable to differences in crystalline environments of **6** compared to either **3** or **5**. The two iron ions in the cations of **3** are crystallographically equivalent. This lets the energy of the two vibronic states of each cation, i.e., $Fe_a^{II}Fe_b^{III}$ and $Fe_a^{III}Fe_b^{II}$, become equal. Tunneling is facilitated. The relatively slow rate in **6** reflects the fact that the I_3^- ion is positioned next to the nearest cation such that it is closer to one iron ion than the other. The resulting energy inequivalency of the two vibronic states considerably reduces the rate of tunneling or, for that matter, the rate of thermally activated electron transfer.

Several other samples of environmental control of the rate of electron transfer can be cited for **1**–**8**. In isostructural salts such as **3** and **4**, it has been found that a change in the anion impacts on the rate of electron transfer.[5,6] Complex **3** is valence detrapped on the Mössbauer time scale at 4.2 K, whereas complex **4** has to be heated to 80 K to become detrapped on the Mössbauer time scale.

The influence of the anion and intermolecular interactions are quite subtle in **1**, **7**, and **8**.[7–9] These complexes are valence trapped at low temperatures but become detrapped when the sample temperature is increased to a certain value. The presence of phase transitions is indirectly indicated by appreciable sample history dependencies[8] in the Mössbauer spectra and in the anion dependence[5,6] of the electron-transfer rate. Definitive evidence for the presence of a phase transition in **1** was very recently obtained.[10] The heat capacity at constant pressure, C_p, was measured from 10 to 360 K to find a heat capacity effect with a maximum at 328 K. This is significant, for it is in this same temperature region where Mössbauer data indicate the rate of intramolecular electron transfer is increasing in **1**. Of course, the cooperativity, which is the essence of a phase transition, is determined by intermolecular interactions in the solid state. It is important to realize that complexes **1**, **7**, and **8** are comprised of segregated stacks of mixed-valence cations, where each cation stack is surrounded by four stacks of anions.[8] In contrast, the packing arrangement in **3**–**5** is dominated by alternating stacks of anions and cations.[4] The

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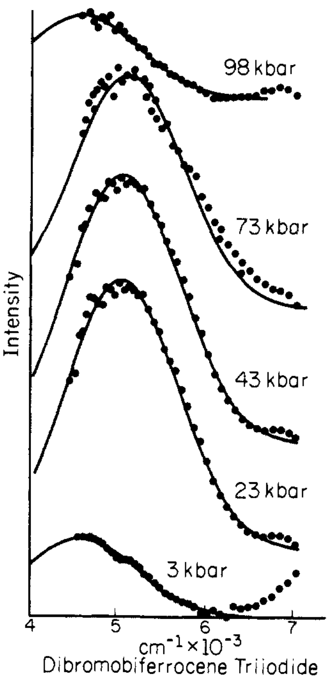

Figure 1. Near-IR electronic absorption spectrum of microcrystalline 1',1'''-dibromobiferrocenium triiodide, compound **5**, measured at various pressures. Mineral oil was used as a pressure-mediating medium.

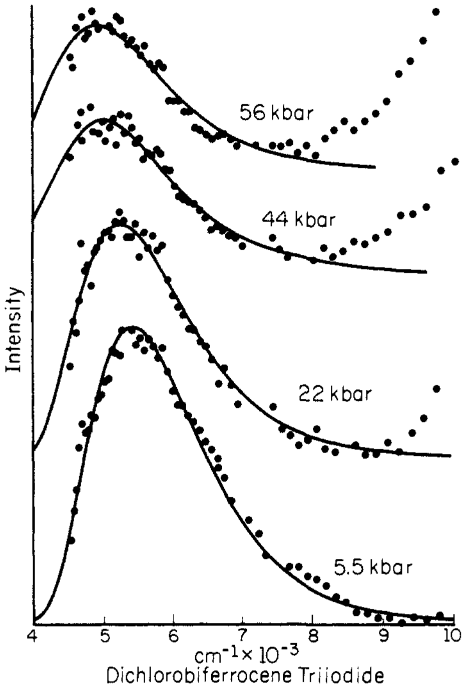

Figure 2. Near-IR electronic absorption spectrum of microcrystalline 1',1'''-dichlorobiferrocenium triiodide hemiiodine, compound **6**, measured at various pressures. Mineral oil was used as a pressure-mediating medium.

magnitudes of intermolecular interactions within stacks and between stacks determine the nature of the cooperative onset of intramolecular electron transfer in the solid state.[11]

In a previous paper[12] it was found that pressure-tuning spectroscopy (PTS)[13] could be used to establish the presence of *intra*molecular and *inter*molecular effects on the electronic structure of the mixed-valence bis(fulvalene)diiron cation. The energy and intensity of the intervalence-transfer (IT) electronic absorption band observed in the NIR were monitored as the externally applied pressure was increased to 141 kbar. In the present paper PTS is used to delineate further the nature of environmental effects on the electronic structure of complexes **1–8**.

Experimental Section

Solid-state electronic absorption spectra were recorded with the samples loaded into an inconel-gasketed diamond-anvil cell, by the ruby fluorescence method of pressure calibration.[14] A 100-W Oriel quartz tungsten–halogen lamp equipped with a Kratos 0.25-m monochromator with 2100 blaze gratings at a slit width of 1 mm was used. Transmitted light was detected by an Opto-Electronics PbS photoconductor. Light pipes were used to connect the diamond-anvil cell to monochromator and the PbS cell. The PbS cell was operated at a 100-V dc bias. A light chopper was placed between the light source and the monochromator. The ac component of the PbS cell was measured with a PAR Model 8 lock-in amplifier.

Samples of compounds **1–8** were prepared according to literature procedures.[3,5,6,8] Good microanalytical data were obtained. The clay-intercalated samples of the biferrocenium and 1',1'''-diethylbiferrocenium cations were prepared by stirring a benzene solution of the natural Fe^{II} metallocene slurried with a synthetic mica–montmorillonite clay (SSM from the Source Clay Mineral Repository). After approximately 24 h the clay takes on the blue color characteristic of the mixed-valence cation. The clay was then washed well with benzene to remove any unoxidized material. The clay-intercalated samples of biferrocenium and 1',1'''-diethylbiferrocenium cations have been characterized by powder X-ray diffraction, EPR, and ^{57}Fe Mössbauer spectroscopy.[15]

Results and Discussion

Pressure Effects on the IT Electronic Absorption Band. In Figures 1 and 2 are given representative NIR electronic absorption spectra obtained at various pressures for microcrystalline samples of 1',1'''-dibromobiferrocenium triiodide (**5**) and 1',1'''-dichlorobiferrocenium triiodide hemiiodine (**6**). The intervalence-transfer (IT) band in each spectrum was least-squares fit to a Gaussian curveform. In this way the value for the energy of the band maximum, E_{max}, was evaluated from each spectrum. The ambient-pressure E_{max} values for the compounds studied were found to range from 4.4 kK for **3** to 5.6 kK for **6**. The lowest energy accessible with the present experimental setup is 4.5 kK. As a consequence, in several cases the full IT band contour could not be recorded (see Figures 1 and 2). Since it was not possible to extend the spectrum over the entire IT band, we could not extract accurate quantitative information about the integrated band intensity as a function of pressure. It is also not possible to discuss changes in band shape with pressure with any precision. It is clear, however, from approximate measurements that, in general, the area under the peak *increased* as the peak shifted to higher energy and *decreased* as it shifted to lower energy.

It should be noted that all of the pressure changes observed were found to be reversible and reproducible. Furthermore, as can be seen in Figure 2, the tail of a second absorption band appears at pressures above 20 kbar for the I_3^- salts. This tail shifts to lower energy and increases in intensity with pressure. It is probably the tail of a charge-transfer band for the I_3^- anion, for it appears in the spectra of all the I_3^- salts and it is known that many charge-transfer peaks involving iodine shift to lower energy with pressure. This tail disappeared reversibly on release of the pressure.

The effect of externally applied pressure on E_{max} for the IT bands of microcrystalline samples of compounds **1–8** and the biferrocenium and 1',1'''-diethylbiferrocenium cations adsorbed into the interlamellar region of a synthetic mica–montmorillonite clay was studied at pressures up to 150 kbar. The data are tabulated in the supplementary material. Before we discuss these results in detail, two general comments should be made. First, it is apparent that E_{max} for the IT band of a given mixed-valence

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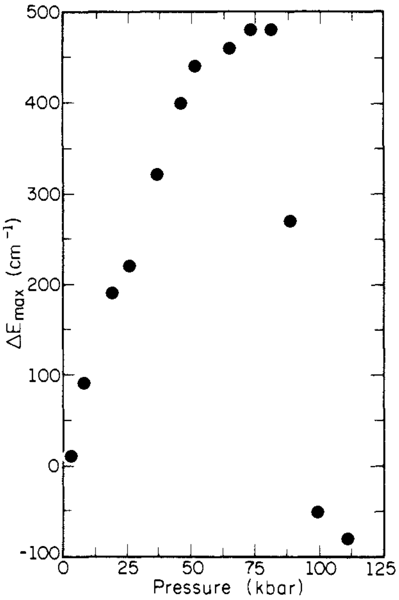

Figure 3. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of 1',1'''-diiodobiferrocenium triiodide, compound **3**.

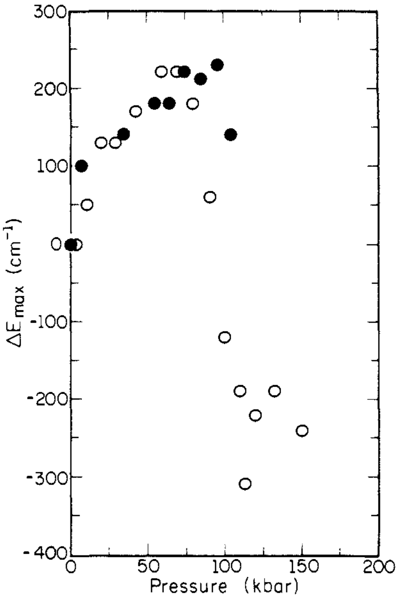

Figure 4. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of 1',1'''-diiodobiferrocenium dibromoiodate, compound **4**. Two independent determinations (filled and unfilled symbols) were performed.

cation is dependent upon the environment (I_3^- salt or clay) in which the cation is located. Second, there seem to be three different types of pressure dependencies, reflecting differences in intermolecular interactions that grow out of differences in packing arrangements in the solid state.

The first type of pressure dependence of E_{max} is found for compounds **3**–**5**. Figures 3–5 illustrate the change in the band maximum energy, ΔE_{max}, as a function of pressure for these three compounds. Upon application of pressure, the IT bands for these three complexes shift to higher energies. The initial rate of change of E_{max} with pressure is ~8 cm^{-1}/kbar for **3** and **5** and ~3 cm^{-1}/kbar for **4**. This blue shift continues up to a pressure of 80 kbar. Upon further increase in the pressure, the IT band abruptly undergoes a pronounced red shift at 25 cm^{-1}/kbar for all three of these compounds.

Microcrystalline samples of the compounds **1**, **2**, and **6**–**8** exhibit a second type of pressure dependence of E_{max}. Inspection of the data presented in Figures 6–10 shows that the IT band for these compounds shifts to lower energies (red shift) with increasing pressure. There is no initial blue shift of the IT band as observed for compounds **3**–**5**. The rate at which the IT band shifts red with increasing pressure varies from one compound to another for **1**, **2**, and **6**–**8**.

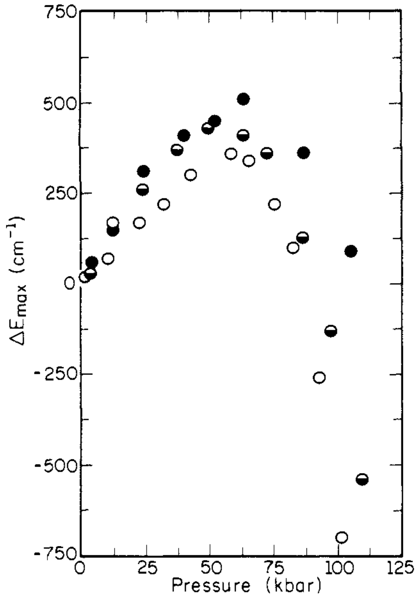

Figure 5. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of 1',1'''-dibromobiferrocenium triiodide, compound **5**. Three independent determinations (filled, unfilled, and half-filled symbols) were performed.

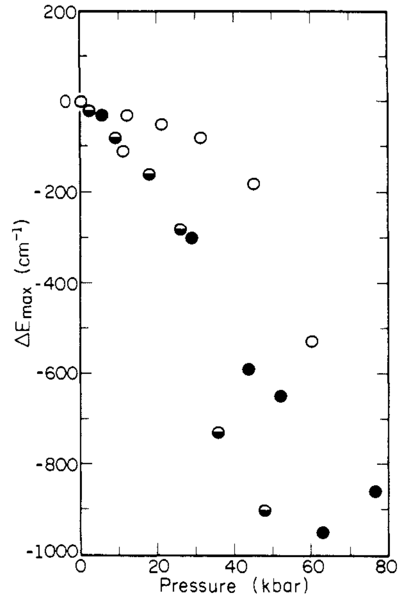

Figure 6. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of 1',1'''-dichlorobiferrocenium triiodide hemiiodine, compound **6**. Three independent determinations (filled, unfilled, and half-filled symbols) were performed.

A third type of pressure dependence was observed for the mixed-valence biferrocenium and 1',1'''-diethylbiferrocenium cations intercalated in the clay. Figure 11 gives a plot of ΔE_{max} versus pressure for these two samples. The pressure shift of the IT band of these two clay-intercalated cations is similar to that reported[12] for the mixed-valence bis(fulvalene)diiron cation intercalated into the same clay. The IT band for the clay-intercalated biferrocenium cation shifts blue with pressure at 2.7 cm^{-1}/kbar (i.e., slope of a least-squares-fit line with a correlation coefficient of 0.97) over the entire pressure range studied. The IT band of the clay-intercalated 1',1'''-diethylbiferrocenium cation also shifts to higher energy with increasing pressure but at a lesser rate. Initially the rate is 1.1 cm^{-1}/kbar, but it decreases significantly at higher pressures.

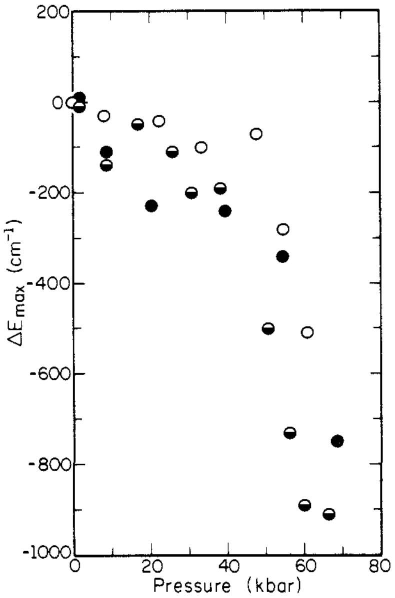

Figure 7. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of biferrocenium triiodide, compound **1**. Three independent determinations (filled, unfilled, and half-filled symbols) were performed.

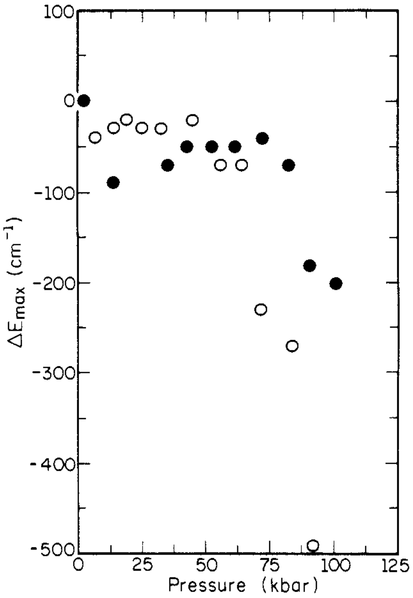

Figure 8. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of biferrocenium hexafluorophosphate, compound **2**. Two independent determinations (filled and unfilled symbols) were performed.

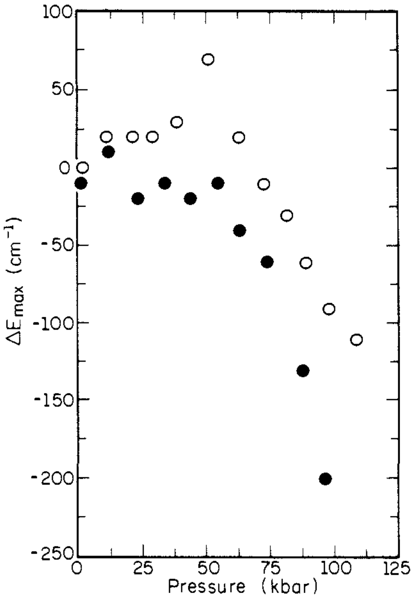

Figure 9. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of 1′,1‴-diethylbiferrocenium triiodide, compound **7**. Two independent determinations (filled and unfilled symbols) were performed.

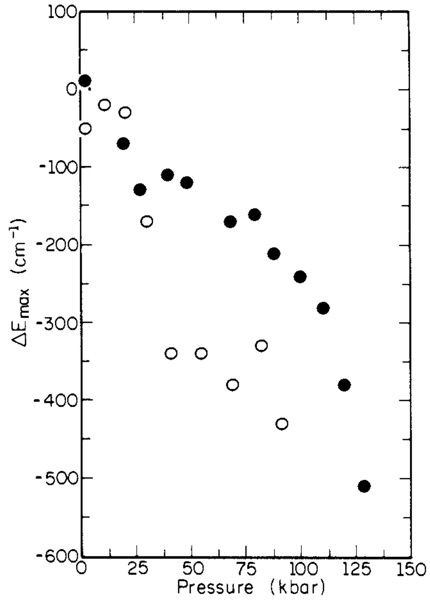

Figure 10. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of 1′,1‴-dibutylbiferrocenium triiodide, compound **8**. Two independent determinations (filled and unfilled symbols) were performed.

Solid-State Environments. The three different types of pressure dependencies observed for the IT bands of compounds **1**–**8** and the clay-intercalated cations can be directly related to the solid-state environment about the mixed-valence cations. Compounds **3**–**5** crystallize in the monoclinic space group *C*2/*m*.[3,4,6] The packing arrangement consists of one-dimensional arrays of cations and anions stacked in an alternating fashion. In the case of **3** the most significant interactions linking cations and anions in these alternating stacks occur between end iodine atoms of the I_3^- anions and the cyclopentadienyliodine atoms of the cation. This I···I contact distance is 3.98 Å.

On the other hand, compounds **1**, **7**, and **8** are known to crystallize in the *P*1̄ space group.[7,8,16] The packing arrangement in these three complexes consists of segregated stacks of cations and I_3^- anions. Each stack of cations is surrounded by four stacks of I_3^- anions. The arrangement of the cations in a stack has a stair-step appearance. In the case of **1** there is an appreciable intercation interaction in the form of an intermolecular $C_5H_5^-$···$C_5H_5^-$ contact with an interplanar distance of 3.4 Å. Compound **8** with its large *n*-Bu substituent experiences an intercation interaction resulting from the *n*-Bu group of one cation contacting the cyclopentadienyl ligand of the other cation.

Compound **6** crystallizes in the space group *I*2.[3] As with all of these complexes the mixed-valence cation in **6** has the trans conformation pictured. The cation in **6** has a valence-trapped $Fe^{II}Fe^{III}$ description as the result of the positioning of the nearest I_3^- anion closer to one iron atom than the other in the cation. There are no alternating stacks of cations and I_3^- anions or segregated stacks of cations and anions evident in the packing arrangement of **6**. The X-ray structure of compound **2** is not known.

The solid-state environment about the mixed-valence biferrocenium and 1′,1‴-diethylbiferrocenium cations, which have been sorbed into the interlamellar region of the mica–montmo-

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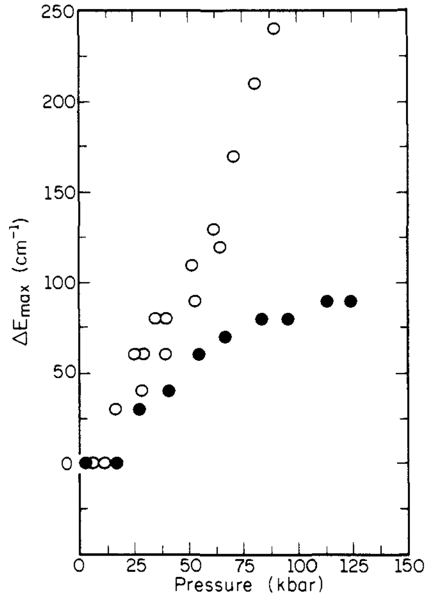
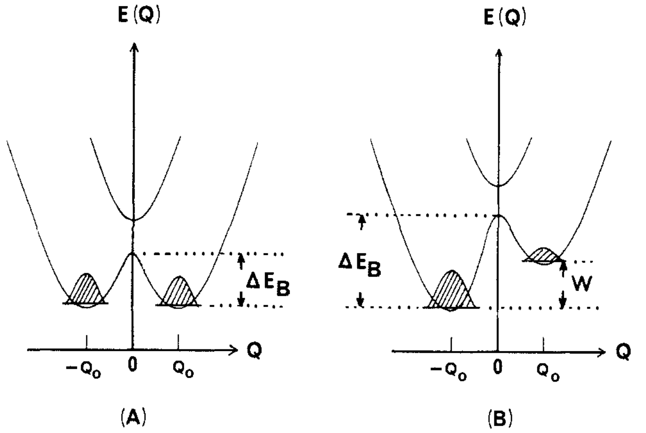


Figure 11. Pressure dependence of the change in energy of the IT band maximum (ΔE_{max}) measured for the IT band of the biferrocenium cation (open circles) and the 1′,1‴-diethylbiferrocenium cation (filled circles) intercalated into a synthetic mica–montmorillonite clay.

rillonite clay, is not totally characterized. These clay-intercalated cations were formed by first sorbing the unoxidized metallocenes into the interlamellar region of the clay. The high Brønsted acidity of the aluminosilicate interlamellar region presumably leads to an acid-catalyzed O_2 oxidation of the metallocenes to give the mixed-valence cations. The counteranions for the mixed-valence biferrocenium and 1′,1‴-diethylbiferrocenium cations are either the anionic aluminosilicate surface of the clay or OH^- from the reduction of O_2. If these two mixed-valence cations assume the trans conformation (pictured above), which has been found in all other compounds, then it is likely that these mixed-valence cations will be oriented in the interlamellar region such that the planes of the cyclopentadienyl and fulvalenide ligands are perpendicular to the clay sheets. EPR experiments on an oriented sample of the mixed-valence bis(fulvalene)diiron cation intercalated in the same synthetic mica–montmorillonite clay did show that this cation assumes one orientation in the clay interlamellar region.[15] The nature of the clay-intercalated mixed-valence biferrocenium and 1′,1‴-diethylbiferrocenium cations was probed by ^{57}Fe Mössbauer spectroscopy and in the latter case by powder X-ray diffraction (XRD). At 4.2 K the biferrocenium cation in the synthetic mica–montmorillonite clay (used because this clay is low in iron content) exhibits two equal-area quadrupole-split doublets in its Mössbauer spectrum. One doublet with a quadrupole splitting (ΔE_Q) of 2.148 (7) mm/s and an isomer shift (δ) of 0.517 (3) mm/s vs iron foil is characteristic of an Fe^{II} metallocene, whereas ΔE_Q = 0.494 (12) mm/s and δ 0.510 (6) for the other doublet indicate an Fe^{III} metallocene. These two doublets confirm the presence of the mixed-valence biferrocenium cation in the clay. In the case of the clay-intercalated 1′,1‴-diethylbiferrocenium cation, equal-area Fe^{II} and Fe^{III} doublets are also seen at low temperatures. At temperatures above ~125 K a third average-valence doublet with ΔE_Q = 0.880 (44) mm/s and δ 0.363 (22) mm/s at 125 K appears and grows in intensity at the expense of the other two doublets when the temperature is increased. Thus, the clay-intercalated mixed-valence 1′,1‴-diethylbiferrocenium cation is converting from valence trapped at low temperatures to valence detrapped at high temperatures. However, at 300 K not all of these mixed-valence cations have become detrapped, only 76% become detrapped as indicated by the relative amounts of the different Mössbauer signals.

Powder XRD measurements were carried out on the clay-intercalated (SWY-1 mica–montmorillonite clay) 1′,1‴-diethylbiferrocenium sample and on an oven-dried sample of the same clay. From the broad peaks in the powder XRD patterns (typical for clays), the interlamellar spacing of the dried clay was found to be in the range of d_{001} = 9.7–10.5 Å. The powder patterns for the clay-intercalated mixed-valence cation sample gave d_{001} = 13.4–14.7 Å. The maximum increase in the interlamellar spacing upon intercalation is 5.0 Å. If, as seems likely, the 1′,1‴-diethylbiferrocenium cation assumes a trans conformation, then the above observation is strong evidence that the clay-intercalated 1′,1‴-diethylbiferrocenium cation is positioned with the plane of the cyclopentadienyl ligands perpendicular to the clay layers.



(A) (B)

Figure 12. Potential energy plotted as a function of the out-of-phase combination of the two symmetric metal–ligand breathing vibrational modes on the halves of a binuclear mixed-valence complex. Diagram A is for a symmetric mixed-valence complex in the absence of environmental effects. Diagram B results if the environment about the binuclear mixed-valence complex is asymmetric.

Origin of the Pressure Shifts of the IT Band. In the case of compounds **1** and **3–8**, it has been definitively established that the mixed-valence cations in these complexes are valence trapped on the IR time scale.[4–6,8] This means, of course, that these cations do have a barrier for electron transfer present in their potential energy diagrams as pictured in Figure 12. In such a diagram the potential energy, $E(Q)$, of a mixed-valence binuclear cation is plotted as a function of the out-of-phase combination, Q, of the two totally symmetric ring–Fe–ring stretching modes, one on each of the metallocene units. The IT band results from an electronic transition from the lower to the upper surface in Figure 12. The environment about a given mixed-valence biferrocenium cation can be symmetric or asymmetric relative to the two iron ions in the cation. If the environment is the same for the two iron ions, the ground-state double-well potential energy surface will be symmetric as indicated in Figure 12A. In this case there are two PKS vibronic model[17] parameters needed to describe the diagram: (1) the electronic coupling parameter (ϵ), which gauges the resonance interaction (avoided crossing) of the two vibronic states; (2) the vibronic coupling parameter (λ). The parameter λ gauges how strongly the two electronic states $Fe_a^{II}Fe_b^{III}$ and $Fe_a^{III}Fe_b^{II}$ couple to the vibrational mode Q. This is reflected by the horizontal displacement, Q_0–($-Q_0$), of the two vibronic minima in Figure 12A.

If the anions are asymmetrically disposed about the mixed-valence cation or there is some other environmental asymmetry, the ground-state potential energy surface will be asymmetric as indicated in Figure 12B. There is in this case a zero-point energy difference (W) between the vibronic states. The introduction of this zero-point energy difference will increase the thermal barrier for electron transfer, or if the main mechanism for *intra*molecular electron transfer is tunneling, then the introduction of a nonzero W will also have appreciable effects on the rate of tunneling. It must be emphasized that intermolecular interaction in the solid state can lead to an appreciable value of W and, as a consequence, valence trapping.[11]

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Compression of crystals consisting of molecular units or large molecular ions leads primarily to a decrease in intermolecular distances. There will also be changes in bond lengths which, while small, can be important. For example, significant changes in vibrational stretching frequencies with pressure have been reported.[18,19] An electronic transition for a molecular moiety will either shift to higher or lower energy, depending on the balance between intramolecular and intermolecular effects.

In terms of the parameters for the PKS vibronic model[17] a compression that leads to a decrease in bond lengths should lead to an increase in the electronic coupling parameter ϵ. This will increase E_{max} associated with an IT band, because the higher energy surface in Figure 12A would move to higher energy relative to the lower energy surface as the pressure is increased.

Another intramolecular effect of increasing the pressure on a mixed-valence cation could be a reduction in the intramolecular vibronic coupling as the pressure is increased. Vibronic coupling in a binuclear mixed-valence biferrocenium cation parallels the difference in normal coordinates of the totally symmetric ring-Fe-ring stretch for the Fe^{II} and Fe^{III} metallocene moieties. Moreover, this difference parallels a difference in the Fe^{II}-ligand and Fe^{III}-ligand bond lengths. The Fe^{III}-C bond length in a mononuclear Fe^{III} metallocene has been reported[20] to be 2.075 Å, while the Fe^{II}-C bond length in ferrocene has been reported[21] to be 2.033 Å. The frequencies of the antisymmetric Cp-Fe-Cp stretching vibration for mononuclear Fe^{II} and Fe^{III} metallocenes are 478 and 405-423 cm^{-1}, respectively.[22] This leads to force constants of 2.63 and 1.89-2.06 mdyn/Å, respectively.[22] It is therefore reasonable to assume that the Fe^{III}-C bond is more compressible than the Fe^{II}-C bond and that the difference in bond lengths would decrease with pressure. Thus, an increase in pressure would reduce the vibronic coupling. Such a reduction in coupling would lead to a red shift of the IT peak.

An increase in intermolecular interactions resulting from the application of pressure could lead to an increase in the zero-point energy difference, W, between the two vibronic states (see Figure 12B). It is very likely that such a nonzero W value, which is due to intermolecular interactions, is the main factor leading to valence trapping in the solid state of binuclear mixed-valence complexes, which in the absence of such environmental effects would be valence detrapped (i.e., fast electron and/or nuclear tunneling) because of their symmetric construction.[11]

The pressure dependence of the IT band for the alternating stack compounds **3**-**5** can be explained in view of the above general comments. It is suggested that the initial blue shift at a rate of ~8 cm^{-1}/kbar for **3** and **5** and ~3 cm^{-1}/kbar for **4** could be due to an increase in the zero-point energy W as the pressure is increased. It is to be recalled that compounds **3** and **5** exhibit a rate of intramolecular electron transfer that is fast on the ^{57}Fe Mössbauer time scale ($>10^7$ s^{-1}) even at 4.2 K.[3] Thus, even though they are stacked in an alternating fashion and seem to have appreciable in-stack anion-cation interactions, they must have very small zero-point energy differences (W) because they tunnel at an appreciable rate even at 4.2 K. In fact, only compounds **3** and **5** are valence detrapped on the Mössbauer time scale at 4.2 K. Compound **4** shows the next lowest valence-detrapping temperature of all of the compounds **1**-**8**. As compound **4** is heated from 4.2 K, it becomes valence detrapped on the Mössbauer time scale at ~80 K.[3] Thus, when pressure is initially applied to **3**-**5**, it is quite possible that W begins to increase, and this leads to a blue shift of the IT band. The reduced rate (~3 cm^{-1}/kbar) of blue shift for **4** compared to the rate for **3** and **5** (~8 cm^{-1}/kbar) could reflect the fact that there is a larger value of W at ambient pressure for **4** than for either **3** or **5**. This larger W value for **4** could reflect a stronger cation-anion interaction due to the greater electronegativity of the terminal trihalide atoms of the $Br-I-Br^-$ anion in **4** compared to the terminal atoms of the $I-I-I^-$ anion in **3** and **5**.

Some indirect substantiation for the above suggestion that W increases initially as pressure is increased on compounds **3**-**5** can be gleaned from the IR and EPR data base for compounds **1**-**8**.[3,5,6,8] When the anion is changed for an alternating stack compound such as **3**, **4**, or **5**, the g values in the EPR spectrum and the quantum of the ring-metal-ring asymmetric stretching vibration change for the mixed-valence cation. A change in the anion for segregated stack compounds such as **1**, **7**, and **8** or, for that matter, the other compounds **6** and **2** does *not* lead to a change in the EPR and IR characteristics of the mixed-valence cation. This implies that only in the case of the alternating stack compounds **3**-**5** is it possible to affect appreciably the zero-point energy difference between the two vibronic states.

The segregated stack compounds **1**, **7**, and **8**, as well as **2** and **6**, show either little shift at low pressures or a red shift of the IT band. It is interesting that all of the microcrystalline compounds **1**-**8** exhibit a significant red shift of their IT bands at high pressures. The alternating stack compounds **3**-**5** show an abrupt change from blue shift to red shift of the IT band above a pressure of ~80 kbar. It is possible that this abruptness reflects the achievement of a pressure above which there is no more change in W, and the effect that leads to the red shift of the IT band becomes predominant.

The red shift of the IT band, which starts at various pressures for compounds **1**-**8** is likely due to vibronic coupling decreasing as the pressure is increased. There is a tendency for the difference between the Fe^{II}-ligand and Fe^{III}-ligand bond lengths to decrease at a rate that accelerates drastically above 40-70 kbar, depending on the compressibility of the compounds.

Somewhat different responses of the IT band to applied pressure are seen for the mixed-valence 1′,1‴-diethylbiferrocenium and biferrocenium cations intercalated into clay (see Figure 11). In the latter case the IT band shifts blue linearly with pressure at 2.7 cm^{-1}/kbar up to 90 kbar. In the former case the initial rate of blue shift is only 1.1 cm^{-1}/kbar, and above ~85 kbar, E_{max} does not change much with pressure up to 124.7 kbar. The blue shift of the IT band, which is seen for these mixed-valence cations intercalated in the clay, could be attributable to W increasing with pressure. Upon compression of the clay, the aluminosilicate sheets carrying the negative charge are pushed down upon the mixed-valence cations. Depending on the orientation of the cations in the interlamellar region and the distribution of charge on the clay layer, the compression of the anionic clay layer upon the mixed-valence cations could well introduce a zero-point energy difference.

The absence of a red shift of the IT band for the clay-intercalated mixed-valence cations is also probably understandable. It would seem reasonable that the two different mixed-valence cations assume the same trans conformation in the clay interlamellar region that they have in all salts. Steric interactions in the form of H···H contacts essentially preclude the cis conformation. As substantiated above, these trans-conformation mixed-valence cations are positioned in the interlamellar region such that the planes of the cyclopentadienide and fulvalenide ligands are perpendicular to the aluminosilicate layers. Thus, under applied pressure, the layers of the clay will be pushed closer together. If the compression is anisotropic in this sense, then the vibronic coupling for these clay-intercalated mixed-valence cations may *not* be dramatically affected. This is true if the compression is anisotropic such that there is little compression of the Fe^{II}-C and Fe^{III}-C bonds.

Conclusions and Comments

Three different types of pressure responses of the IT band for mixed-valence 1′,1‴-disubstituted biferrocenium cations have been seen. The three different responses seem to reflect the different solid-state environments of alternating stacks of cations and anions, segregated stacks of cations, and cations intercalated into the interlamellar region of a layered aluminosilicate. The initial blue

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shifting of the IT band seen for the alternating stack and clay-intercalated cations is attributable to an increase in the zero-point energy difference between the two vibronic states of the mixed-valence cation. This results from intermolecular interactions enhanced by pressure.

The red shift of the IT band that dominates the high-pressure response is attributable to an intramolecular effect, namely a reduction of the vibronic coupling in the mixed-valence cation. Thus, under high pressures, the difference between Fe^{II}–C and Fe^{III}–C bond lengths is reduced, which reduces the vibronic coupling.

The major conclusion from this study is that the physical properties of these mixed-valence biferrocenium cations depend strongly on the solid-state environments. It would be quite interesting to monitor the rate of electron transfer of such a mixed-valence complex as the applied pressure is increased. This could be done indirectly by spectroscopic means such as ^{57}Fe Mössbauer spectroscopy.

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Supplementary Material Available: Tables I–VII of changes of $E_{\max}$ vs pressure data for the IT bands (7 pages). Ordering information is given on any current masthead page.

Stereochemistry of Crown Ethers and Their Complexes in the Solid State. ^{13}C CPMAS NMR and X-ray Crystallographic Studies of Configurationally Isomeric Dicyclohexano-14-crown-4 Ethers, Dibenzo-14-crown-4 Ether, and Some Lithium Thiocyanate Salts

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Abstract: For the cis-anti-cis and cis-syn-cis isomers of dicyclohexano-14-crown-4 and one LiNCS complex, X-ray crystallographic data are presented along with solid-phase ^{13}C NMR spectra. Clear evidence for inversion of one of the cyclohexane rings of the cis-syn-cis isomer in order to form the LiNCS complex is presented. Other structural features of these systems are discussed in detail as well as the geometrical dependence of ^{13}C chemical shifts in solids. For the dibenzo-14-crown-4 complex with LiNCS the solid-phase ^{13}C NMR spectral results are discussed in light of the known X-ray structure.

In crown ether chemistry, the 14-crown-4 system is of interest because of its nearly ideal cavity dimensions for complexation of the lithium ion. For the parent 14-crown-4 ether molecule, the X-ray crystal structure, determined at −150 °C, has been published.[1] For dibenzo-14-crown-4, the structure of its LiNCS complex has also been determined via X-ray techniques.[2] By contrast, little is known regarding the solid-state structure of dicyclohexano derivatives of the 14-crown-4 system.

Recently[3,4] we have found that solid-phase ^{13}C NMR is a powerful method for the determination of asymmetric units in a series of dicyclohexano-18-crown-6 ethers. Interpretation of such spectra, however, can be complicated by crystal packing phenomena or the existence of different crystal forms in the solid.[5] Hence inclusion of available X-ray data in any discussion of ^{13}C CPMAS spectra is required.

With the solid-phase ^{13}C chemical shifts in hand along with the corresponding X-ray data, the opportunity exists for detailed analysis of stereochemical contributions to carbon shieldings.

Results and Discussion

The structural formulae and numbering schemes for the molecules studied herein are depicted in Figure 1. The numbering schemes employed are chosen to be consistent with the X-ray data output rather than with IUPAC convention. Bond lengths and angles for *cis-anti-cis*-dicyclohexano-14-crown-4 (**1**), the corresponding cis-syn-cis isomer **2**, and the LiNCS complex of **2** are listed in Table I. Torsion angles involving ring skeletal atoms for these three systems are provided in Table II along with data for 14-crown-4 itself. Figure 2 shows stereoviews of **1**, **2**, and the LiNCS complex of **2** while Figure 3 contains the ^{13}C CPMAS spectra of these systems. In Figure 4 are presented the ^{13}C CPMAS spectra of dibenzo-14-crown-4 and its LiNCS complex. Table III contains the ^{13}C solid-phase chemical shifts for the five systems examined herein.

(i) ***cis-anti-cis*-Dicyclohexano-14-crown-4 (1).** In solution,[6] under low-temperature conditions where ring inversion is slow on the ^{13}C NMR time scale, this molecule has been shown to exist as a mixture of two conformations in the ratio of ca. 2:1. The ^{13}C CPMAS spectrum (Figure 3) of solid **1**, however, suggests the presence of only one conformation in the crystal, since only nine resonances are observed.

Figure 2 shows that **1** has a local center of symmetry from the molecular standpoint. Averages over pairs of presumed symmetry related non-hydrogen positions of **1** were calculated and yielded

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